

Disjoining Pressure for Non-uniform Thin Films

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It is known that the concept of the disjoining pressure between two parallel interfaces due to van der Waals interactions cannot generally be extended to films of non-uniform thickness. We derive a formula for the disjoining pressure for a film of non-uniform thickness by minimizing the total Helmholtz free energy for a thin film residing on a solid substrate. The disjoining pressure for a thin film of small slope on a flat substrate is shown to take the form:

$$\Pi = -A_{123}(4 - 3h_x^2 + 3hh_{xx}) / 24\pi h^3$$

where A_{123} is the Hamaker constant for a phase 1 and 2 interacting through a phase 3; h , h_x , and h_{xx} are the local film thickness, slope, and second order derivative, respectively.

Our work is concerned with a generalization of the theoretical approach, pioneered by Lifshitz and discussed more recently by Israelachvili, for the inclusion of van der Waals forces in a theoretical framework suitable for the dynamics of thin liquid films via the introduction of the so-called *disjoining pressure*.

In the continuum mechanics view, interfaces or boundaries between two macroscopic phases are treated as pure mathematical surfaces of zero thickness and zero mass. The macroscopic property of interfacial tension or interfacial free energy per unit area accounts for the difference in the collective molecular interaction effects for a heterogeneous system containing a fluid interface with respect to those interactions that would exist if the system were a homogeneous one. In a macroscopic multi-phase system, in which all phase boundaries and interfaces are sufficiently far apart, the incorporation of interfacial tension into the stress balance at fluid interfaces, together with the condition of continuity of velocities across the interface, produce a complete set of boundary conditions for free-surface problems. These conditions, together with the macroscopic Navier-Stokes equations, provide a basis for description of fluid motion and interface shapes. However, if the distance between interfaces or boundaries approaches

the mesoscopic regime (~ 100 nm or less), the collective effect of molecular interactions across these mesoscopic regions must be taken into account.

A rational revision is the *disjoining pressure* approximation, which was originally developed by Lifshitz for the case in which the mesoscopic region takes the form of a thin film. In this approach, which applies strictly for two unbounded parallel and flat interfaces or boundaries, the “additional” intermolecular forces between the phases across the film are replaced by an attractive force per unit area, which can be thought of as a pressure applied at the boundaries of the film, namely the so-called *disjoining pressure*:

$$\Pi = -A / 6\pi h^3$$

where h is the distance between the two parallel, sharp interfaces and A is the Hamaker constant, which can be evaluated via the Lifshitz theory. The simple concept of disjoining pressure between two parallel interfaces has been applied in a number of papers to study the stability and rupture of thin (but non-uniform) liquid films. However, as already noted, the simple formula for the disjoining pressure is exact only for thin films of uniform thickness. Moreover, as argued in some references, when the film thickness is very small, $h \rightarrow 0$, the classical formula for the disjoining pressure becomes unbounded. This leads to problems with the description of a thin film ending on a substrate and prevents determination of the motions near the edge of the film.

In our work, we have chosen to utilize a definition of the disjoining pressure based on Yeh’s thermal equilibrium condition for a liquid thin film residing on a flat solid substrate, but we modify it to include the excess energy outside the film. Assuming a van der Waals hard sphere interaction, we integrate the intermolecular potential throughout the whole heterogeneous system and obtain the excess energy associated with the disjoining pressure by subtracting the interfacial tension potential from the total intermolecular potential. In the limit of a small slope, the disjoining pressure given by this approach takes the relatively simple form:

$$\Pi = -A_{123}(4 - 3h_x^2 + 3hh_{xx}) / 24\pi h^3$$

where A_{123} is the Hamaker constant for the interactions between phase 1 and 3 through phase 2 and h , h_x , and h_{xx} are the local film thickness, slope, and second-order derivative, respectively. A key point is that the form for the Hamaker constant depends on the properties of all three phases, and is completely consistent with Lifshitz theory for non-retarded van der Waals forces.

The extension to more general non-uniform thin films which are not necessarily bounded by a solid substrate is more or less trivial, and can be achieved by constructing tangential planes along the top and the corresponding bottom interfaces of the film.

One needs to be very careful when trying to extrapolate the concept of disjoining pressure, basically a mesoscopic concept, to molecular scales. The main problem arises from the characteristic length scales at which molecules are prevented from overlapping because of steric effects. Such steric effects automatically preclude extrapolation of the thickness of the film to zero values; they actually provide a minimum thickness which is of the order of molecular dimensions. On the other hand, in disjoining pressure analyses that start with a film thickness that is much larger than molecular length scales, the distinction between molecular scales and a film of zero thickness is usually ignored. But if the film thickness becomes comparable to molecular scales, the molecular size can no longer be neglected.

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